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(54) Title: IMPROVEMENTS IN OR RELATING TO A METHOD FOR TRANSESTERIFYING VEGETABLE OILS

(57) Abstract: The invention relates to a method for producing Diesel grade fuel of plant origin by transesterifying a refined vegetable oil with a C1-C4 alkanol in the presence of a catalyst whereupon a polar phase and an apolar phase is formed, removing the polar phase comprising glycerol by-product, and subjecting the apolar phase comprising the fuel to a refining procedure. According to the method of the invention refined vegetable oil is transesterified in a homogeneous phase in the presence of at least 0.2 parts by volume, related to unit volume of refined vegetable oil, of an aliphatic hydrocarbon solvent with a boiling point of 40-200°C to form a mixture comprising a polar phase and an apolar phase, if necessary, the apolar phase which also comprises non-transesterified vegetable oil beside aliphatic hydro-carbon solvent and transesterified product, obtained after removing the separated polar phase comprising glycerol by-product, is reacted in a further step with a C1-C4 alkanol in the presence of a catalyst until a transesterification conversion of 95-98 % is attained, the separated polar phase comprising glycerol by-product is removed, and the apolar phase comprising the fuel is refined wherein, if desired, at least a portion of the aliphatic hydrocarbon solvent is retained in the product



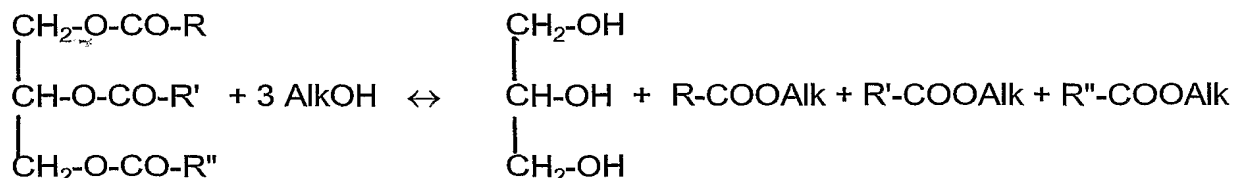
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## IMPROVEMENTS IN OR RELATING TO A METHOD FOR TRANSESTERIFYING VEGETABLE OILS

The invention relates to improvements in or relating to a method for transesterifying vegetable oils. More particularly, the invention relates to an improved method for producing Diesel grade fuel of plant origin (also termed in the following as biodiesel fuel or biodiesel) by transesterifying vegetable oils with C1-C4 alkanols (further on: alkanols).

As known, transesterification with an alkanol has a decisive influence on the quality of fuels produced from vegetable oils, because it depends basically on this operation whether the viscosity of the resulting fuel fits for injecting and engine driving purposes or not.

Transesterification of vegetable oils with an alkanol proceeds in a reversible equilibrium reaction according to the scheme



- in the formulae R, R' and R'' stand for the hydrocarbyl moieties of the fatty acid constituents of vegetable oils and Alk is a C1-C4 alkyl group. As it appears from the above scheme, glycerol is formed as by-product in the reaction in addition to the fatty acid methyl esters usable as fuel. The equilibrium can be shifted towards the formation of the required fatty acid alkyl esters by increasing the amount of the alkanol reactant and/or by removing the glycerol by-product. Transesterification is performed generally in the presence of a catalyst. Usually bases are applied as

catalysts (most frequently potassium hydroxide); acid catalysts are used less frequently. As alkanol most frequently methanol is used.

A classical method for transesterifying vegetable oils with methanol and for producing biodiesel fuel on this basis have been disclosed in US patents Nos. 2,360,844, 2,383,632 and 2,383,633; this is the method which has been generally used, with some minor modifications, for the production of biodiesel fuel on industrial scale till now. According to the method disclosed in the cited references vegetable oil is reacted with methanol in the presence of potassium hydroxide catalyst for at least one hour at a temperature below the boiling point of methanol (usually at 65°C). As methanol and vegetable oil have only limited miscibility in each other, the biphasic reaction mixture is intensely stirred and/or phase transfer catalysts are used in order to accelerate the reaction. Glycerol, which liberates as a by-product, accumulates in the polar (methanol) phase, and - in accordance with the equilibrium nature of the reaction - is prone to reconvert the once-produced fatty acid methyl esters into glyceride esters. The phase transfer catalyst optionally present assists this reversion process, too, thus no full conversion of the vegetable oil can be attained. When the reaction mixture is close to equilibrium, which corresponds to a conversion of about 80 %, the mixture is allowed to settle for about one day. Thereafter the lower polar phase (which comprises glycerol together with the major portion of methanol used in excess) is removed, and the reaction is repeated with the upper apolar phase with freshly admixed alcohol and catalyst. After this second step the upper apolar phase (fuel phase) is separated again, subjected to distillation to remove part of the methanol contained therein, washed with aqueous sulphuric acid to remove potassium hydroxide, washed again with water, dried and filtered (this latter series of operation is consisting the refining of biodiesel fuel). If desired, quality

improving additives, particularly additives improving cold resistance, are added to the resulting biodiesel fuel.

Major disadvantages of the above method are as follows: due to the biphasic mixture the reaction requires a lengthy period of time and an energy consuming intense stirring to proceed; separation of the phase which contains glycerol by-product is difficult and extremely time consuming; methanol should be used in a great excess to the stoichiometric amount in order to shift the reaction towards the formation of the required product; the majority of non-reacted methanol appears in the glycerol phase from which it cannot be recovered in an economic way unless acceptable operational capacity was employed. In a paper discussing the improvement potentials of biodiesel transesterification fuel production (D. Darnoko and M. Cheryan: JAOCS 77, 1269-1272 (December, 2000)) the authors mention as further disadvantages that the method requires large reactor volumes and repeated start up/shut down cycles resulting increase in capital and labour investments and decrease in production efficiency, furthermore the quality of the product may vary from batch to batch.

According to US patents No. 5,520,708 and 6,015,444 the time required for transesterification and phase separation is reduced by performing the reaction in an assembly of a static mixer, a heat exchanger, a homogenizer and a settling vessel rather than using a conventional reaction vessel equipped with a stirrer. The static mixer used in this method, like all static mixers, does not contain moving means for mixing the reactants; a turbulent flow created either by flow-breaking means (such as baffles, ribs, coils etc.) mounted inside the mixer or by a packing filled into the mixer serves to mix the reactants intensely. Vegetable oil, alkanol (most frequently methanol) and catalyst are passed through the static mixer, the resulting dispersed

stream is heated to reaction temperature in the heat exchanger, thereafter the mixture is subjected to a high shear in the homogenizer to form an emulsion, and the emulsion is passed into the settling vessel where no further stirring is applied. The lifespan of the emulsion formed in the homogenizer enables transesterification to proceed to equilibrium conversion before the emulsion segregates in the settler. Although a significant reduction in time requirement can be attained with this method, it is a disadvantage that a homogenizer with high energy consumption should be used. Again, this method does not enable to attain a conversion higher than the equilibrium in a single step, thus in order to attain 95-98 % conversion required to obtain a product with appropriate viscosity the apolar phase should be reacted once again. The alkanol should be used in such a great excess which is unacceptable for industrial scale production.

According to the method disclosed in DE 42,09,779 the required conversion of about 98 % is attained by performing transesterification in a column divided into reaction zones and separation zones, each reaction zone being followed by a separation zone. Vegetable oil, alkanol and catalyst are fed into the first reaction zone, then after a prescribed period of time the resulting mixture is fed into the first separation zone for removing glycerol by centrifuging. The resulting glycerol-free mixture is fed then into the second reaction zone, and the above reaction/separation steps are repeated in series until the required conversion is attained. An important advantage of this method is that it can also be performed as a continuous operation, because the time consuming settling is replaced by the much faster centrifugal separation. This advantage is, however, overcompensated by the extreme high installation investments which render the method too expensive. Therefore this method is not applied in plants with a capacity lower than 100,000 tons/year. As a further disadvantage,

this method cannot be applied for transesterifying vegetable oils containing more than 2 % of free fatty acids.

In order to avoid the disadvantages associated with heterogeneous reactions, particularly in order to decrease reaction time and energy demand of stirring, it has also been suggested to transesterify vegetable oils with alkanol under homogeneous reaction conditions [*www.bioxcorp.com. with reference to Production of a cost-competitive biodiesel fuel alternative to petroleum diesel, in Environmental Science & Engineering, May, 2001.*]. According to this attempt a polar solvent well soluble both in the polar alkanol and in the apolar vegetable oil (such as tetrahydrofuran or N-methyl-2-pyrrolidin-one) have been utilized as reaction medium. However, such a method requires very complicated and energy consuming separation steps for processing the final reaction mixture, which overcompensates the advantages resulting from the use of a homogeneous mixture. Namely, due to a change in phase conditions, after transesterification the polar solvent distributes between the biodiesel phase with increased apolarity and the glycerol phase with increased polarity and should be removed from both phases. The disadvantages arising from the equilibrium nature of the reaction cannot be avoided with this method, since glycerol is continuously present in reactive state in the reaction mixture for transesterification. Thus this solvent assisted method has not been utilized on industrial scale.

Publications relating to biodiesel fuel production state that efficient transesterification, which is imperative for obtaining a product with the required quality, requires the use of refined vegetable oil as starting substance. This holds particularly when the vegetable oil is a waste (e.g. spent frying oil). No specific method for refining vegetable oils has been disclosed, however, in publications relating to bio-

diesel fuel production. According to the known technologies for producing food grade products, vegetable oils are refined by treating them with water to remove hydratable phospholipids and with acids, like phosphoric acid or citric acid, to remove non-hydratable phospholipids [*Hoffman, G.: Chemistry and technology of edible oils and fats and their high fat products, Academic Press, London ; Toronto, 1989*]. The resulting refined vegetable oils (termed in food technology as "degummed oils") are suitable starting substances for biodiesel fuel production. From the aspects of transesterification proceeding in heterogeneous phase it is an advantage that such refined (degummed) vegetable oils contain a series of minor components with some surfactant properties. In the method of US patents Nos. 5,520,708 and 6,015,444 cited above just these vegetable oil components are utilized to form an emulsion. At the same time the difficulties arising at the separation of the apolar phase comprising transesterified substances from the polar phase comprising glycerol by-product can be attributed to the presence of these components.

Our aim was to perform improvements in transesterification, a key step of biodiesel fuel production. Our primary aim was to elaborate a method which enables one to reduce considerably the time requirements of transesterification and subsequent glycerol removal, without, however, requiring expensive equipment or complicated processing steps for this purpose. Our further aim was to elaborate a method which enables one to reduce considerably the alkanol requirement of transesterification without affecting conversion and to attain the required conversion of 95-98 % without time-consuming intermittent glycerol separation steps.

It has been found, unexpectedly, that the primary aim can be achieved fully when an aliphatic hydrocarbon (which term covers cycloaliphatic and cycloaliphatic-aliphatic hydrocarbons, too) with a boiling point of 40-200°C or a mixture of such

hydrocarbons is used as reaction medium in the alkanol transesterification of the vegetable oil in an amount of at least 0.2 parts by volume related to unit volume of the starting refined vegetable oil.

Thus, in one aspect, the invention relates to an improved process for producing Diesel grade fuel of plant origin by transesterifying a refined vegetable oil with a C1-C4 alkanol in the presence of a catalyst whereupon a polar phase and an apolar phase is formed, removing the polar phase which comprises glycerol by-product, and subjecting the apolar phase which comprises the fuel to a refining procedure. According to the invention refined vegetable oil is transesterified in a homogeneous phase in the presence of at least 0.2 parts by volume, related to unit volume of refined vegetable oil, of an aliphatic hydrocarbon solvent with a boiling point of 40-200°C to form a mixture comprising a polar phase and an apolar phase, if necessary, the apolar phase which also comprises non-transesterified vegetable oil beside aliphatic hydrocarbon solvent and transesterified product, obtained after removing the separated polar phase comprising glycerol by-product, is reacted in a further step with a C1-C4 alkanol in the presence of a catalyst until a transesterification conversion of 95-98 % is attained, the separated polar phase comprising glycerol by-product is removed, and the apolar phase comprising the fuel is refined.

Thus the basic difference between the method according to the invention and the known methods wherein transesterification is performed in a homogeneous reaction mixture resides in that a specific apolar solvent is used to form the homogeneous reaction mixture instead of using a polar solvent. The aliphatic hydrocarbons used as apolar solvents according to the invention have the unique property that they can dissolve the polar alkanol in an amount required in the reaction, but they dissolve the glycerol by-product (which is also an alcohol and also a polar sub-



stance) to a very limited degree. Thus the mixture for transesterification remains homogeneous during the full course of the reaction, which enables the reaction to proceed quickly. At the same time, as the reaction proceeds, glycerol accumulates in a distinct polar phase, which fully separates from the apolar phase within a short period of time. By an appropriate feeding of the alkanol it can also be attained that only a small amount of alkanol is dissolved in the polar phase, thus only a small loss in alkanol is caused by the removal of the polar phase. Thereby the amount of alkanol required in transesterification can be reduced significantly.

Transesterification is performed at a temperature of 60-140°C, preferably at 95-115°C, under a pressure sufficient to maintain the alkanol in liquid state. Any of the conventional catalysts usable for transesterification can be applied in the method of the invention. Potassium hydroxide proved to be a particularly preferred catalyst. The pressure may be 1-40 bar.

The lower limit of the amount of the aliphatic hydrocarbon solvent is a critical value. We have also observed that the minimum amount of aliphatic hydrocarbon solvent required to form a homogeneous phase in transesterification also varies with the nature of the starting vegetable oil and with the method used to refine the vegetable oil. When the vegetable oil has been refined according to the method of the invention, which method will be discussed later, for certain vegetable oils even 0.2 parts by volume of aliphatic hydrocarbon solvent may be sufficient to form a homogeneous phase in transesterification, whereas when the vegetable oil has been refined by an other method (e.g. by an aqueous-acidic treatment discussed above), the minimum amount of aliphatic hydrocarbon required to form a homogeneous phase in transesterification may be greater (usually 0.3-0.4 parts by volume, related to unit volume of refined plant oil). The required minimum amount of aliphatic hydro-

carbon solvent can easily be determined experimentally. When raising the amount of the aliphatic hydrocarbon solvent above the critical lower limit, the time required for full separation of the polar and apolar phase decreases. However, the upper limit of the amount of the aliphatic hydrocarbon solvent is not a decisive factor, and depends primarily on economic considerations. We have found that no particular advantages arise from raising the amount of the aliphatic hydrocarbon solvent above the twofold of the amount of the starting refined vegetable oil. The volume ratio of the starting refined vegetable oil to the aliphatic hydrocarbon solvent may be preferably 1:(0.2-1.5), more preferably 1:(0.3-1), particularly 1:(0.4-0.7).

As aliphatic hydrocarbon solvents preferably substances with boiling points of 60-180° or mixtures of such substances can be used (when a mixture is used, the figures represent boiling ranges). Mineral oil cuts of low aromatic content with boiling ranges of 60-100°C, 100-140°C and 140-180°C proved to be particularly preferable.

We have also found that a solution obtained as upper apolar phase upon admixing a non-refined vegetable oil with an aliphatic hydrocarbon solvent boiling at 40-200°C and with aqueous glycerol and allowing the mixture to settle can be applied particularly preferably in the process according to the invention instead of using refined vegetable oil and aliphatic hydrocarbon solvent as separate streams. Said upper apolar phase is in fact a solution of refined vegetable oil in the respective aliphatic hydrocarbon solvent. According to this vegetable oil refining method, which is adapted specifically to the transesterification method of the invention, unit volume of non-refined vegetable oil is thoroughly admixed with at least 0.2 parts by volume (preferably 0.2-1.5, more preferably 0.3-1, particularly 0.4-0.7 parts by volume) of an aliphatic hydrocarbon solvent with a boiling point of 40-200°C and with 0.07-0.2 parts by volume (preferably 0.09-0.15 parts by volume) of aqueous glycerol compris-

ing 5-40 % by volume (preferably 10-20 % by volume) of water, the mixture is allowed to settle to form a lower polar phase and an upper apolar phase, and the upper apolar phase, which is a solution of the refined vegetable oil in the aliphatic hydrocarbon solvent, is transferred then to transesterification. Using this refining method impurities and components which disturb transesterification and subsequent separation can be removed from the vegetable oil much more efficiently than by the known method discussed above. A particular advantage of the vegetable oil refining method according to the invention is that minor components with surfactant properties, which cannot be removed from the vegetable oil with the conventional aqueous-acidic refining, are also removed, which further accelerates the separation of the polar and apolar phases formed in transesterification. A further important advantage of the refining method according to the invention is that no foreign substance is introduced into the process, since the aliphatic hydrocarbon solvent is the same as that utilized as reaction medium in transesterification, and the glycerol is the by-product formed in transesterification.

Transesterification can be performed according to the invention in a reaction vessel, usually in an autoclave equipped with a stirrer and with a heating jacket, conventionally used for transesterification, according to the two-step method well known from the literature. In this instance the aliphatic hydrocarbon solvent, the refined vegetable oil (or a preformed solution thereof, e.g. the upper apolar phase obtained in the above refining step), the alkanol and the catalyst (or a preformed solution thereof) are introduced, and the mixture is stirred at the prescribed reaction temperature. When the reaction is performed under atmospheric pressure, the temperature of the reaction must not exceed the boiling point of the alkanol. However, the reaction can also be performed at higher temperatures under superatmospheric pressure,

provided that the alkanol remains in liquid state. The reaction can be performed at a temperature of 60-140°C under a pressure of 1-40 bar. Applying elevated temperature under superatmospheric pressure the speed of reaction can be further increased. When transesterification reaction has reached the steady (equilibrium) state, heating and stirring is stopped, pressure is reduced to atmospheric if necessary, and the phases are allowed to separate. We have observed that the steady state sets in within a short time (sometimes even within 10 minutes), and the separation of the phases is also quick (full separation occurs sometimes even within 10 minutes). The polar lower phase, consisting mainly of glycerol together with a small amount of alkanol) is removed, and subjected to known glycerol processing operations, if desired. The upper apolar phase, which contains some unreacted vegetable oil together with the aliphatic hydrocarbon solvents and the fatty acid alkyl esters formed in transesterification, is then subjected to a second transesterification step as described above to attain the required 95-98 % conversion. Again, the required reaction time is short (sometimes it is less than 10 minutes). Full separation of the polar lower phase formed in this second step from the upper apolar phase takes usually a longer period of time, it requires, however, much less time than that required in the conventional method. If desired, phase separation can be accelerated by known methods (e.g. by filtering the biphasic mixture through a particulate, porous or sieve-like substance with a solid/liquid surface tension of at least 40 mN/m, such as basalt filling, cotton, metal sieve or ion exchange resin).

It should be noted here that in the first step usually a conversion of 85-88 % (i.e. exceeding somewhat that obtainable in the conventional method) can be attained, despite of the fact that the excess of alkanol, if any, is not higher than 30 %

related to the stoichiometric amount. According to our experiences a higher excess of alkanol is not required.

According to a particularly preferred method transesterification and separation of the polar and apolar phases are performed in an assembly as shown in Fig. 1, which comprises a receiver 1 and a static mixer 2 smaller in volume lower than the receiver, coupled to said receiver as a bypass by pipelines 3 and 4. The receiver serves to receive the aliphatic hydrocarbon solvent and the reactants required for transesterification, or to receive only the refined vegetable oil and the aliphatic hydrocarbon solvent (this latter is the more preferred solution), and to separate the polar and apolar phases from one another, whereas the actual transesterification reaction takes place in the static mixer. In the receiver temperature and pressure are adjusted to ambient values, whereas the static mixer is heated to the prescribed reaction temperature. If it is higher than the boiling point of the alkanol under atmospheric pressure, the pressure prevailing in the static mixer is adjusted with a pressurizing unit (not shown in the Figure) to a value required for keeping the alkanol in liquid state. In this instance a pressure reducer (not shown in the Figure) is installed into pipeline 4 at a point before it enters the receiver. In the static mixer the temperature can be adjusted to 60-140°C (preferably to 95-115°C), whereas the pressure can be adjusted to 1-40 bar (preferably to 20-24 bar). The refined vegetable oil and the aliphatic hydrocarbon solvent (preferably as the upper phase obtained in the vegetable oil refining step according to the invention) are fed into the receiver at a point shown by arrow 5. If desired, the alkanol and the catalyst can also be fed into the receiver, however, it is more preferred to introduce the alkanol and the catalyst at a point shown by arrow 6 into pipeline 3 which connects the receiver with the static mixer, before it enters the static mixer. In transesterification portions of the

mixture fed into the receiver are circulated through the static mixture at a rate which enables transesterification to proceed at least partially in the static mixer. When no alkanol and catalyst have been fed into the receiver, these substances are fed into the stream exiting the receiver at a point shown by arrow 6. One can proceed so that a substance stream is fed batchwise from the receiver into the static mixer, if required, alkanol and catalyst are fed into this stream at a point shown by arrow 6, and after an appropriate period of time the substance stream in the static mixer, which comprises aliphatic hydrocarbon solvent, fatty acid alkyl esters, some non-transesterified vegetable oil, glycerol and catalyst and optionally a small amount of alkanol, too, is reintroduced into the receiver. This procedure is started then again. It is, however, more preferred to feed a substance stream continuously from the receiver into the static mixer at a rate which enables transesterification to proceed at least partially in the static mixer. The term "circulated through the static mixer" encompasses both solutions. If alkanol and catalyst are fed at the point shown by arrow 6, the total amount of alkanol required for transesterification is introduced preferably into the substance stream in portions so that in the initial stage of transesterification the mixture in the static mixer contains the alkanol only in a stoichiometric amount or less, and the amount of added alkanol is raised above the stoichiometric value only when a relatively high conversion (preferably above 80 %) has already been attained. This operation is continued until the required 95-98 % conversion of transesterification is attained.

Since the conditions prevailing in the receiver differ from those prevailing in the static mixer and the mixture in the receiver, from which the polar glycerol phase rapidly separates, is not stirred, transesterification reaction cannot proceed in the receiver, or if yes, only very slowly. This also means that glycerol, separated as a

distinct phase in the receiver, cannot react in the receiver with the fatty acid alkyl esters once formed, reforming thereby the vegetable oil. Thus with this solution, as a result of the continuous separation of glycerol, transesterification reaction is shifted towards the formation of the required fatty acid alkyl esters, and the required 95-98 % conversion can be attained without stopping transesterification, separating the phases, and repeating transesterification in a further step on the apolar upper phase. No significant alkanol excess is required to attain 95-98 % conversion, either. If the alkanol is introduced into the static mixer as a separate stream in portions so that in the initial stage of transesterification less than stoichiometric amounts are introduced and the amount of the added alkanol is raised only after attaining a relatively high conversion, a 95-98 % conversion may be attained even upon using the alkanol in stoichiometric amount. A further important advantage of this method is that it can be performed in a very simple apparatus.

If desired, depending on the dimension of the receiver, portions of the separated polar phase can be removed from the receiver periodically during transesterification.

When the required 95-98 % conversion has been attained, transesterification is stopped, the substance in the receiver is allowed to settle, and the the lower polar phase consisting mainly of glycerol is removed. A portion of the removed glycerol can be recycled in the vegetable oil refining step after admixing it with the required amount of water. If a vegetable oil refined according to the method of the invention is used in transesterification, the purity grade of the resulting glycerol phase is higher than that attainable by the conventional method, thus its further processing is more easy. This is an additional advantage of the method of the invention.

The upper apolar phase obtained at the end of transesterification, which comprises the required biodiesel fuel, is subjected then to refining operations. Conventional steps of refining can be applied. The aliphatic hydrocarbon solvent can also be removed upon refining. However, in some instances, particularly when aliphatic mineral oil cuts with higher boiling ranges have been applied, it is preferred to retain at least a portion of the aliphatic hydrocarbon solvent in the biodiesel fuel product, because these components improve the quality of the fuel (e.g. increase its cetane number and decrease its iodine number).

*A preferred method of refining is disclosed below.*

Refining of the upper apolar phase: The small amount of alkanol is removed by distillation, thereafter the apolar phase is washed with dilute aqueous sulphuric acid and then with water, water introduced with these operations is removed by azeotropic extractive distillation, finally, if desired, the aliphatic hydrocarbon solvent or a part thereof is distilled off. The presence of the aliphatic hydrocarbon solvent considerably simplifies the removal of water during refining.

Refining of the lower polar phase: The alkanol is removed by distillation and the catalyst is removed with a method fitting the nature of the particular catalyst (potassium hydroxide catalyst can be removed as potassium sulphate by sulphuric acid treatment). When neat glycerol is to be prepared, the polar phase is passed then through anion and cation exchange resins. If water has been introduced during refining, this can be removed most efficiently by azeotropic distillation performed in the presence of the aliphatic hydrocarbon solvent and subsequent removal of the solvent residues by distillation.

As it appears from the above, the presence of aliphatic hydrocarbon solvent facilitates refining, too, since in its presence both glycerol and the apolar phase can



be dried (dehydrated) by simple atmospheric distillation. The alkanol and the aliphatic hydrocarbon solvent can be recovered easily in the refining operation and can be recycled into the transesterification step. Portions of the separated polar phase can be recycled into the vegetable oil refining step according to the invention.

The most important advantages of the method according to the invention are as follows:

- transesterification reaction and phase separation proceed quickly;
- the amount of alkanol required for transesterification can be reduced considerably;
- simple apparatuses are required;
- the required 95-98 % conversion can also be attained without an intermittent stopping of transesterification, separating the phases, and performing a repeated transesterification;
- refining of the end product is more simple;
- the solvent and the nonreacted reactants can be recovered easily and can be recycled;
- a biodiesel fuel with an even quality can be produced;
- using appropriately selected aliphatic hydrocarbon solvents, quality improving additives can simultaneously be introduced into the biodiesel fuel product.

Further details of the invention are shown by the aid of the following non-limiting Examples.

#### Example 1

400 ml of cold pressed sunflower oil (kinematic viscosity at 40°C: 32 mm<sup>2</sup>/s; acid number: 1.2 mg KOH/g), 175 ml of an aliphatic hydrocarbon fraction obtained in mineral oil distillation (boiling range: 75-95°C; amount of aromatics: less than 1 %), and a mixture of 40 ml of glycerol and 5 ml of water were fed into a container fitted

with a stirrer, and the contents of the container was stirred for 20 minutes at a rate of 120 rpm. Stirring was stopped, and the contents of the container was allowed to stand for 30 minutes. The separated lower polar phase, which comprises the glycerol, the water and all impurities removed by them, was removed through a discharging unit fitted to the bottom of the container, and the upper apolar phase, comprising 96 % of the introduced vegetable oil and aliphatic hydrocarbon solvent, was filled into a four-necked flask equipped with a stirrer, a reflux condenser, a thermometer and a dropping funnell. Sample was taken from the upper apolar phase for analysis, and the solvent was removed. According to the results the kinematic viscosity of the thus refined solvent-free vegetable oil decreased to 24 mm<sup>2</sup>/s (measured at 40°C); its acid number decreased to 0.1 mg KOH/g.

In a separate flask 2 g of potassium hydroxide was dissolved in 125 ml of methanol, and 75 ml portion of the resulting solution was filled into the dropping funnell. The substance filled into the four-necked flask was heated to a temperature of about 60°C under stirring at a rate of 120 rpm, and then the methanol solution of potassium hydroxide was added dropwise. The progress of transesterification was coupled with a slight increase in temperature. When the addition of the methanol solution was complete (which required 10 minutes) the temperature of the reaction mixture raised to 68°C; thus the reaction reached the equilibrium within 10 minutes. Heating was switched off, and the reaction mixture, cooled to 50°C, was filled into a separation funnell. The lower polar phase fully separated from the upper apolar phase within 12 minutes. The lower polar phase comprising glycerol was set aside, and the upper apolar phase was refilled into the four-necked flask. The remainder of the methanol solution of potassium carbonate (50 ml) was filled into the dropping funnell, and transesterification of the apolar phase was continued as described above. Full

transesterification was attained within 7 minutes. The contents of the flask was filled into a separation funnell, and the phases were allowed to separate at room temperature. Full separation of the phases required 120 minutes.

After both transesterification steps samples were taken from the upper apolar phase, the aliphatic hydrocarbon solvent was removed from the samples by distillation, and then the samples (termed as "biodiesel phase" in Table 1) were analyzed. The results are indicated in Table 1, where the respective data of the starting sunflower oil and of the refined sunflower oil are also given for comparison purposes.

Table 1

	Starting sunflower oil	Refined sunflower oil	Biodiesel phase
Conversion			Step 1: 88.8 % Step 2: 97.9 %
Viscosity at 40°C, mm <sup>2</sup> /s	32	24.1	Step 1: 6.16 Step 2: 4.57
Acid number, mg KOH/g	1.18	0.1	Step 1: 0.2 Step 2: 0.2
Density at 20°C, g/cm <sup>3</sup>	0.921	0.907	Step 1: 0.892 Step 2: 0.881

### Example 2

The procedure of Example 1 was followed with the difference that after both transesterification steps the biphasic mixture was passed through 15 g of an anion-exchange resin in order to accelerate phase separation. Thus the time required for full separation of the phases (indicated by full transparency of the upper phase) decreased for Step 1 to 8 minutes and for Step 2 to 48 minutes. Upon this operation the acid number of the biodiesel phase also decreased to 0.1 mg KOH/g. Kinematic

viscosity of the biodiesel phase obtained in Step 2 was  $4.46 \text{ mm}^2/\text{s}$  (measured at  $40^\circ\text{C}$ ), its density was  $0.880 \text{ g/cm}^3$  (measured at  $20^\circ$ ), which, compared with the respective data of Table 1, indicates that, regarding the characteristics decisive from the aspects of usability, biodiesel fuel can be prepared by the method of the invention in a steady quality.

### Example 3

One boring each was formed on the bottom and on the middle of the sidewall of a three-necked flask of 2 litres capacity, and pipelines for material supply, equipped with a closing valve, were fitted to the individual borings. A collector flask was placed below the pipeline fitted to the boring on the bottom. A tube equipped with a heating jacket was joined through a centrifugal pump to the pipeline fitted to the boring on the sidewall, and the tube was filled with 25 g of anion exchange resin. A pipeline was joined to the upper end of the tube, which was connected to one of the necks of the flask. Thus the assembly shown in Fig. 1, comprising a receiver and a static mixer connected thereto as a bypass, was formed. The flask was fitted with a thermometer and a reflux condenser. 1100 ml of a mixture of refined sunflower oil and aliphatic hydrocarbon solvent, obtained as described in Example 1, and a solution of 4 g of potassium hydroxide in 250 ml of methanol were filled into the flask. A completely homogeneous monophasic liquid was obtained. Water heated to  $75^\circ\text{C}$  was circulated in the heating jacket of the static mixer (i.e. of the tube filled with anion exchange resin), but the flask itself was not heated. The contents of the flask was circulated through the static mixer at a rate of 50 l/min with the centrifugal pump. Upon the effect of the substance stream recirculated into the flask the temperature in the flask started to raise. When the temperature raised above  $45^\circ\text{C}$ , the separation of a polar lower phase was already well observable. When the temperature

in the flask reached 65°C, the closing valve attached to the lower boring was opened, a part of the separated polar phase was removed, and the separated polar phase was removed further at a rate of its formation by adjusting appropriately the closing valve. Steady state, indicated by that no further polar phase separates, was reached within 37 minutes. At this time the lower closing valve was closed, circulation through the static mixer was continued for further 10 minutes, then circulation was stopped, the contents of the flask was allowed to cool to room temperature, and from that time it was allowed to stand at room temperature for 1 hour. Thereafter the lower polar phase was removed through the lower closing valve, and the solvent was removed from the upper apolar phase which remained in the flask. Biodiesel fuel was obtained with a conversion of 96 %. Quality characteristics of the product were as follows: kinematic viscosity at 40°C: 4.36 mm<sup>2</sup>/s; density at 20°C: 0.876 g/cm<sup>3</sup>; acid number: 0.17 mg KOH/g.

#### Example 4

The procedure of Example 3 was followed with the difference that potassium hydroxide used as catalyst was replaced by an equivalent amount of sodium hydroxide. Under such conditions steady state was attained within 52 minutes, and the repose period required for full phase separation raised from 1 hour to 1.7 hours. The biodiesel fuel was obtained with a conversion of 96 %. Quality characteristics of the product were as follows: kinematic viscosity at 40°C: 4.54 mm<sup>2</sup>/s; density at 20°C: 0.884 g/cm<sup>3</sup>; acid number: 0.25 mg KOH/g.

#### Example 5

The procedure of Example 3 was followed with the difference that Blaugel<sup>(R)</sup> (a silica gel which indicates water saturation by colour change) was filled into the static reactor as packing instead of anion exchange resin. Under such conditions

steady state was attained within 41 minutes, and the two phases, like in Example 3, fully separated after standing at room temperature for 1 hour. The biodiesel fuel was obtained with a conversion of 95 %. Quality characteristics of the product were as follows: kinematic viscosity at 40°C: 4.49 mm<sup>2</sup>/s; density at 20°C: 0.880 g/cm<sup>3</sup>; acid number: 0.18 mg KOH/g.

#### Example 6

The procedure of Example 3 was followed with the difference that a four-necked flask was used, and a dropping funnell was fitted into one of the necks. No methanol solution of potassium hydroxide was filled into the flask, but a solution of 4.8 g of potassium hydroxide in 300 ml of methanol was introduced through the dropping funnell in 10 equal portions. The separated polar phase was removed before introducing the individual solution portions. The correct timing of removal of the lower polar phase was determined by the inset of steady state (no more glycerol separates). The biodiesel fuel was obtained with a conversion of 98 %. Quality characteristics of the products were as follows: kinematic viscosity at 40°C: 4.38 mm<sup>2</sup>/s; density at 20°C: 0.879 g/cm<sup>3</sup>; acid number: 0.14 mg KOH/g.

#### Example 7

The procedure of Example 1 was followed with the difference that transesterification was performed in a pressurized reactor at 114°C under a pressure of 24 bar. The 75 ml portion of the 125 ml methanol solution of potassium hydroxide was directly filled into the reactor. The reaction mixture was stirred with a magnetic stirrer. After reaching the required temperature the mixture was stirred for 10 minutes, stirring was then stopped, the temperature of the reactor was lowered to 50°C and the pressure was lowered to atmospheric, and the contents of the reactor was filled into a separation funnell. An immediate full phase separation was

observed, which indicates that the time elapsed after stopping of stirring (about 5-10 minutes) was sufficient to attain full phase separation. The conversion of transesterification (measured in the upper apolar phase after removing the solvent) was 92 %. Quality characteristics of the substance were as follows: kinematic viscosity at 40°C: 5.87 mm<sup>2</sup>/s; acid number: 0.29 mg KOH/g.

Upon subjecting the upper apolar phase to repeated transesterification the biodiesel fuel was obtained with a conversion of 98 %. Quality characteristics of the product were as follows: kinematic viscosity at 40°C: 4.38 mm<sup>2</sup>/s; density at 20°C: 0.879 g/cm<sup>3</sup>; acid number: 0.14 mg KOH/g.

#### Example 8

Spent frying oil was filtered to remove solid impurities amounting to about 3 %. 400 ml of the resulting filtrate (kinematic viscosity at 40°C: 39.8 mm<sup>2</sup>/s; acid number: 3.55 mg KOH/g) were refined as described in the first part of Example 1. Sample was taken from the upper apolar phase obtained in the refining step, and the aliphatic hydrocarbon solvent was removed from the sample. The kinematic viscosity of the resulting refined vegetable oil decreased to 25.6 mm<sup>2</sup>/s (measured at 40°C), its acid number decreased to 0.38 mg KOH/g. No filtration residue was obtained upon filtering the refined vegetable oil.

Thereafter the two-step transesterification procedure described in Example 1 was repeated with the apolar upper phase obtained in the refining step. The conversion attained in the second transesterification step was 96 %. Quality characteristics of the product were as follows: kinematic viscosity at 40°C: 4.66 mm<sup>2</sup>/s; density at 20°C: 0.881 g/cm<sup>3</sup>; acid number: 0.1 mg KOH/g.

What we claim is:

1. A method for producing Diesel grade fuel of plant origin by transesterifying a refined vegetable oil with a C1-C4 alkanol in the presence of a catalyst whereupon a polar phase and an apolar phase is formed, removing the polar phase comprising glycerol by-product, and subjecting the apolar phase comprising the fuel to a refining procedure, characterized in that refined vegetable oil is transesterified in a homogeneous phase in the presence of at least 0.2 parts by volume, related to unit volume of refined vegetable oil, of an aliphatic hydrocarbon solvent with a boiling point of 40-200°C to form a mixture comprising a polar phase and an apolar phase, if necessary, the apolar phase which also comprises non-transesterified vegetable oil beside aliphatic hydrocarbon solvent and transesterified product, obtained after removing the separated polar phase comprising glycerol by-product, is reacted in a further step with a C1-C4 alkanol in the presence of a catalyst until a transesterification conversion of 95-98 % is attained, the separated polar phase comprising glycerol by-product is removed, and the apolar phase comprising the fuel is refined wherein, if desired, at least a portion of the aliphatic hydrocarbon solvent is retained in the product.

2. A method as claimed in claim 1, characterized in that 0.3-1 parts by volume of aliphatic hydrocarbon solvent is used for unit volume of refined vegetable oil.

3. A method as claimed in claim 2, characterized in that 0.4-0.7 parts by volume of aliphatic hydrocarbon solvent is used for unit volume of refined vegetable oil.

4. A method as claimed in any of claims 1-3, characterized in that a substance with a boiling point of 60-180°C or a mixture of such substances is used as aliphatic hydrocarbon solvent.



5. A method as claimed in any of claims 1-4, characterized in that a mineral oil cut of low aromatic content with a boiling range of 60-100°C, 100-140°C or 140-180°C is used as aliphatic hydrocarbon solvent.

6. A method as claimed in any of claims 1-5, characterized in that transesterification is performed at a temperature of 60-140°C, preferably 95-115°C, under a pressure sufficient for maintaining the C1-C4 alkanol in liquid state.

7. A method as claimed in any of claims 1-6, characterized in that methanol is used as C1-C4 alkanol.

8. A method as claimed in claim 1, characterized in that an upper apolar phase obtained by thoroughly admixing unit volume of a non-refined vegetable oil with at least 0.2 parts by volume (preferably 0.2-1.5, more preferably 0.3-1, particularly preferably 0.4-0.7 parts by volume) of an aliphatic hydrocarbon solvent with a boiling point of 40-200°C and with 0.07-0.2 parts by volume (preferably 0.09-0.15 parts by volume) of aqueous glycerol comprising 5-40 % by volume (preferably 10-20 % by volume) of water, allowing the mixture to settle to form a lower polar phase and an upper apolar phase and removing said lower polar phase is used as refined vegetable oil and aliphatic hydrocarbon solvent.

9. A method as claimed in any of claims 1-8, characterized in that transesterification and removal of the polar phase comprising glycerol by-product is performed in an assembly comprising a receiver and a static mixer coupled to said receiver with pipelines as a bypass so that the receiver is maintained at ambient temperature and pressure, the temperature and pressure prevailing in the static mixer are adjusted to those required for transesterification reaction, the refined vegetable oil and the aliphatic hydrocarbon solvent, furthermore optionally also the C1-C4 alkanol and the catalyst are fed into the receiver, portions of the contents of the re-

ceiver are circulated through the static mixer at a rate which enables transesterification to proceed at least partially in the static mixer, whereby, when no C1-C4 alkanol and catalyst have been fed into the receiver, these substances are fed into the stream exiting the receiver before it enters the static mixer, this operation is continued until a 95-98 % conversion of transesterification is attained, thereafter circulation is stopped, and the polar phase separated at the bottom of the receiver is removed.

10. A process as claimed in claim 9, characterized in that portions of the polar phase separated at the bottom of the receiver are also separated during circulation.

11. A process as claimed in claim 1, characterized in that water which has been introduced into the apolar phase with the refining operations is removed by subjecting the apolar phase to azeotropic distillation in the presence of the aliphatic hydrocarbon solvent.

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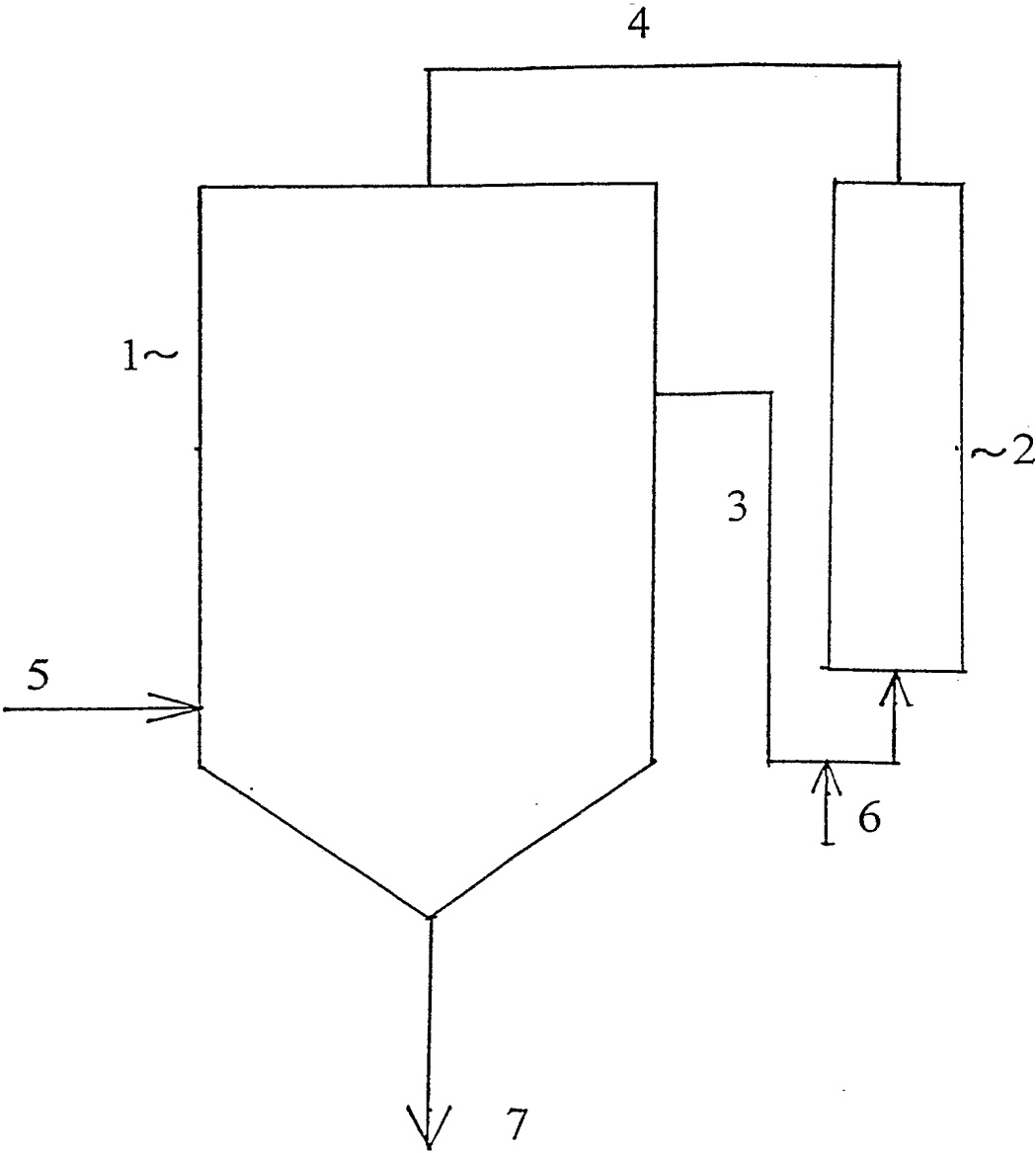


Fig. 1

# INTERNATIONAL SEARCH REPORT

International Application No

PC1/HU 02/00114

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/03 C11C3/00 C10L1/02 C11C3/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11C C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, FSTA, COMPENDEX, BIOSIS, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 12581 A (BOOCCOCK DAVID GAVIN BROOKE) 22 February 2001 (2001-02-22) page 6, paragraphs 3,4 page 8, paragraphs 4-8 claims 1-23; examples 1-6	1-4,6-11
Y	---	5
Y	US 5 219 733 A (MYOJO KATSUNORI ET AL) 15 June 1993 (1993-06-15) column 23, line 10-18	5
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

3 March 2003

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26/03/2003

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# INTERNATIONAL SEARCH REPORT

International Application No

PC 1 / HU 02/00114

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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